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Relationes

Comment on the Extended Hückel Method Applied to Transition Metal Complexes

P. W. Smith, R. Stoessiger and A. G. Wedd
Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia

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It is indicated that the effects of neglecting 1. the inter-atomic electrostatic field effects (M_i) and 2. the correction required to compensate the off-diagonal elements for the constant potential $-Z$ implicitly included by approximating the diagonal elements as VSIE's largely cancel. To the extent that this cancellation holds, previous EH calculations may be rationalised in this regard.

It has become obvious from recent work [1] that the simple Extended Hückel (EH) approach to the electronic structure of transition metal complexes is inadequate and that much more detailed calculations are necessary. Any success claimed for the EH method must be largely due to cancellation of errors and it would be useful if some of the sources of this cancellation could be defined.

The diagonal matrix elements H_{ii} in the LCAO approach are of the form:

$$H_{ii} = H_{ii}^{\mathrm{A}} + M_i \qquad (1)$$

where i indicates a given atomic orbital, A denotes atomic energy terms, H_{ii}^{A} is the term characteristic of the free atom and M_i is the effect of the fields of the neighbouring atoms. The H_{ii}^{A} terms are usually estimated as valence state ionisation potentials (VSIE) [2].

Early approaches [3, 4] neglected the M_i term inherent in the diagonal matrix element [5, 6] and led to a prediction of high covalencies in transition metal oxide and halide complexes. This is at variance with experimental evidence. Cotton and Harris [7] found that an arbitrary decrease in the charge dependence of the VSIE's resulted in improved agreement with experiment.

In general, the effect of the M_i terms is to modify both the neutral atom value of the VSIE and its dependence upon charge q_i, i.e. M_i can be represented by:

$$M_i = M_i(q_i = 0) + M_i(q_i)\,. \qquad (2)$$

The first term depends upon the magnitude of the overall charge on the complex ion and is zero in uncharged species (e.g. $TiCl_4$). Fenske [8] has pointed out that in some highly-charged ions (e.g. $CrCl_6^{3-}$), the magnitude of $M_i(q_i = 0)$ is such that H_{ii} can become positive and lead to computational difficulties. These can be overcome if a constant potential $-Z$ is added to the Hamiltonian of the problem. The diagonal element then becomes $(H_{ii} - Z)$ and the calculation is unchanged, provided the off-diagonal element H_{ij} changes by $(-Z S_{ij})$, where S_{ij} is the overlap integral between orbitals i and j. A strong criticism [8] of some formulae for off-diagonal elements is that they do not follow the above behaviour, when a constant potential is included.

The great majority of EH calculations have employed the Mulliken-Wolfsberg-Helmholz (MWH) approximation [3] for the off-diagonal element:

$$H_{ij} = F\,S_{ij}(H_{ii} + H_{jj})/2 \tag{3}$$

where F is a numerical parameter or some closely allied form. This was derived from the Mulliken approximation for *potential* energies only:

$$V_{ij} = S_{ij}(V_{ii} + V_{jj})/2\,. \tag{4}$$

Now

$$H_{ij} = T_{ij} + V_{ij} \tag{5}$$

where V_{ij} and T_{ij} are the potential and kinetic energy contributions respectively. Eq. (3) has been criticised [8] on the grounds that a multiplicative factor, F, has been used for an additive correction.

However, Eq. (3) can be written

$$H_{ij} = S_{ij}(H_{ii} + H_{jj}) + (F-2)\,S_{ij}(H_{ii} + H_{jj})/2\,. \tag{6}$$

Consider the case in which the H_{ii}'s are approximated by atomic VSIE's i.e. $M_i = 0$. As noted by Cusachs and Cusachs [9], VSIE's obey the virial theorem, and thus

$$T_{ii}^{\mathrm{A}} = -\tfrac{1}{2}\,V_{ii}^{\mathrm{A}}\,. \tag{7}$$

Also

$$H_{ii}^{\mathrm{A}} = T_{ii}^{\mathrm{A}} + V_{ii}^{\mathrm{A}} \tag{8}$$

and therefore

$$H_{ii}^{\mathrm{A}} = \tfrac{1}{2}\,V_{ii}^{\mathrm{A}} = -T_{ii}^{\mathrm{A}}\,. \tag{9}$$

Substituting Eq. (9) into Eq. (6) gives:

$$H_{ij} = S_{ij}(V_{ii}^{\mathrm{A}} + V_{jj}^{\mathrm{A}})/2 + (2-F)\,S_{ij}(T_{ii}^{\mathrm{A}} + T_{jj}^{\mathrm{A}})/2 \tag{10}$$

$$= V_{ij}^{\mathrm{A}} + (2-F)\,S_{ij}(T_{ii}^{\mathrm{A}} - T_{jj}^{\mathrm{A}})/2 \tag{11}$$

by Eq. (4). Thus, by Eq. (5),

$$T_{ij} = (2-F)\,S_{ij}(T_{ii}^{\mathrm{A}} + T_{jj}^{\mathrm{A}})/2\,. \tag{12}$$

Ruedenberg [10] has shown empirically that for some orbitals

$$T_{ij} = S_{ij}^2(T_{ii}^{\mathrm{A}} + T_{jj}^{\mathrm{A}})/2 \tag{13}$$

is a good approximation. It is interesting to note that in most EH calculations, the value of F used (1.6–2.0) is such that $(2-F)$ is of the order of S_{ij}.

Now, as noted above, the H_{ii}'s are much better represented by Eq. (1), than by the VSIE's only. The explicit inclusion of the coulombic potential M_i can have no effect on the kinetic energy terms. Thus Eq. (12) is unchanged. However, Eq. (4) becomes, still applying the virial theorem to atomic terms only,

$$V_{ij} = S_{ij}(V_{ii}^{\mathrm{A}} + M_i + V_{jj}^{\mathrm{A}} + M_j)/2$$

$$= S_{ij}(2H_{ii}^{\mathrm{A}} + M_i + 2H_{jj}^{\mathrm{A}} + M_j)/2\,.$$

That is

$$V_{ij} = S_{ij}(H_{ii}^{\mathrm{A}} + H_{jj}^{\mathrm{A}}) + S_{ij}(M_i + M_j)/2\,. \tag{14}$$

Now

$$\begin{aligned} H_{ij} &= V_{ij} + T_{ij} \\ &= S_{ij}(H_{ii}^{\mathrm{A}} + H_{jj}^{\mathrm{A}}) + S_{ij}(M_i + M_j)/2 \\ &\quad + (2-F)\,S_{ij}(T_{ii}^{\mathrm{A}} + T_{jj}^{\mathrm{A}})/2 \\ &= S_{ij}(H_{ii}^{\mathrm{A}} + H_{jj}^{\mathrm{A}}) + S_{ij}(M_i + M_j)/2 \\ &\quad + (F-2)\,S_{ij}(H_{ii}^{\mathrm{A}} + H_{jj}^{\mathrm{A}})/2\,. \end{aligned}$$

That is

$$H_{ij} = F S_{ij}(H_{ii}^{\mathrm{A}} + H_{jj}^{\mathrm{A}})/2 + S_{ij}(M_i + M_j)/2\,. \tag{15}$$

Should a constant potential $-Z$ be added to the Hamiltonian, then considerations similar to those employed to obtain Eq. (14) and Eq. (15) require:

$$H_{ij} = F S_{ij}(H^{A}_{ii} + H^{A}_{jj})/2 + S_{ij}(M_i + M_j)/2 - Z S_{ij}. \tag{16}$$

Thus use of Eq. (15) allows a constant potential to be added to the Hamiltonian for any value of F. If Eq. (3) is used, this is possible only for $F = 1$ [8].

The Cusachs off-diagonal approximation [9] is claimed to result in a distinct improvement in semi-empirical calculations [11]. It invokes the Mulliken potential energy approximation (Eq. (4)) and the Ruedenberg kinetic energy approximation (Eq. (13)). In the same way, this approximation becomes

$$H_{ij} = S_{ij}(2 - |S_{ij}|)\,(H^{A}_{ii} + H^{A}_{jj})/2 + S_{ij}(M_i + M_j)/2 - Z S_{ij}. \tag{17}$$

Consider the case when the M_i's are of the same order for all the basis orbitals. If we choose $Z = (M_i + M_j)/2 \sim M_i$, the diagonal element assumes a value close to that of the VSIE, while the off-diagonal element, Eq. (16), reduces to the classical MWH form.

The Table lists values of $M_i(q_i = 0)$ and $M_i(q_i)$ from Eq. (2) for basis orbitals plausibly included in a calculation on CrCl_6^{3-}. They were estimated using the Fenske modification of the Shullman-Sugano electrostatic approximation (see Ref. [6]). This appears a reasonable approximation for ionic compounds. If Z is taken as 150 kK, there will be large cancellation of the $M_i(q = 0)$ terms. However, the $M_i(q_i)$ terms will still remain. These are essentially positive and effectively reduce the size of the off-diagonal element and thus the interaction of the relevant orbitals. This must lead to reduced covalency.

Table. *M_i factors for* CrC_6^3

Atom	Orbital	$M_i(q_i = 0)$	$M_i(q_i)$
Cr	$3d\ (t_{2g})$	148.4	$49.5 \times q(\mathrm{Cr})$
	$3d\ (e_g)$	150.1	$50.5 \times q(\mathrm{Cr})$
	$4s$	144.8	$48.3 \times q(\mathrm{Cr})$
	$4p$	137.7	$48.9 \times q(\mathrm{Cr})$
Cl	$3s$	148.4	$131.6 \times q(\mathrm{Cl})$
	$3p_z$	160.5	$153.9 \times q(\mathrm{Cl})$
	$3p_x$	143.0	$86.3 \times q(\mathrm{Cl})$

$M_i = M_i(q_i = 0) + M_i(q_i)$. See text. Energies in kilokaysers (kK).

By taking VSIE's as diagonal elements and using the classical MWH formula, Eq. (3), the Wolfsberg-Helmholz [3], and Ballhausen-Gray [4] approaches achieve a large cancellation of the $M_i(q_i = 0)$ terms, but do not include the effect of the $M_i(q_i)$ factors. On the other hand, Cotton and Harris [7] arbitrarily restrain the charge dependence of the VSIE's and thus achieve higher ionic characters for the series of complexes they examined.

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Dr. P. W. Smith
Chemistry Department
University of Tasmania
Hobart 7001, Tasmania, Australia